gebildet waren ausschliesslich (100)-Flächen (Blättchenebene) und (011)-Flächen.

Die Elementarzelle besitzt die Abmessungen:

$$a_0 = 16{,}45 \pm 0{,}02,\ b_0 = 9{,}93 \pm 0{,}035,\ c_0 = 9{,}49 \pm 0{,}02 \text{ Å};\ \beta = 107{,}9 \pm 0{,}2°;\ \alpha = \gamma = 90°.$$

Nimmt man an, dass 2 Moleküle in der Zelle enthalten sind, ergibt eine Berechnung der Dichte 1,163 g.cm.$^{-3}$.

Gemessen: 1,16$_5$ g.cm.$^{-3}$.

Ein Ausschnitt aus dem reziproken Gitter wurde in gleicher Weise wie bei der monomeren Verbindung gewonnen. Es wurde um die ausgezeichnete Achse (*b*-Achse) gedreht und präzessiert. Allgemeine Auslöschungen (*hkl*) traten nicht auf. Die fehlenden Reflexe *h*0*l* mit $l = 2n+1$ und 0*k*0 mit $k = 2n+1$ weisen der Verbindung die Raumgruppe $P2_1/c$ zu.

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Coordinate errors due to rotational oscillations of molecules.

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The writer has shown (Cruickshank, 1956*a*) how molecular angular oscillations can cause the maximum of an atomic peak in the electron density to be displaced towards the centre of rotation. The shift was taken to be in a radial direction and was calculated as

$$\Delta = \tfrac{1}{2}r\left(\frac{s^2}{1+s^2/q^2} + \frac{t^2}{1+t^2/q^2}\right), \tag{1}$$

where r is the distance from the centre of molecular oscillation, s^2 and t^2 are the mean square amplitudes of oscillation of the atom in the rotations about the two principal axes perpendicular to the radius and q^2 is the Gaussian-breadth parameter for the peak before the rotational oscillations are considered. The previous derivation assumed that only angular oscillations about axes perpendicular to the radius were relevant, since the atom is not moved by an oscillation about this radius. This assumption is clearly wrong in general. For if there is an atom at $(x, y, 0)$ and all the elements of the ω_{ij} angular oscillation tensor (Cruickshank, 1956*b*) are zero except ω_{11}, the shift will obviously be towards the x-axis and not towards the origin, so that the maximum will appear at $(x, y-\Delta', 0)$ and not at $\{x(1-\Delta/r), y(1-\Delta/r), 0\}$. Equation (1) evidently gives the total shift only when a principal axis of ω_{ij} coincides with the radius to the atom.

The previous formula was derived by finding the maximum of the electron density along the radius. The general problem is more difficult since the direction of the shift is unknown. An approximate formula is derived below from a centre-of-gravity approach.

Let $\mathbf{r} = (x, y, z)$ be the equilibrium position of an atom and $\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \varphi_3)$ be an arbitrary small rotation of the molecule. Then the combined effect of rotations by $\boldsymbol{\varphi}$ and $-\boldsymbol{\varphi}$ will be to produce a weighted contribution to the total electron density whose maximum will lie on the normal

$$\mathbf{a} = -\mathbf{r} + (\mathbf{r}\,.\,\boldsymbol{\varphi}/\varphi^2)\boldsymbol{\varphi} \tag{2}$$

from the atom to the axis of oscillation and which will be displaced from the equilibrium position by the small amount $\frac{1}{2}\mathbf{a}\varphi^2$. The x component of this displacement is

$$\Delta_x(\boldsymbol{\varphi}) = -\tfrac{1}{2}x(\varphi_2^2+\varphi_3^2) + \tfrac{1}{2}y\varphi_1\varphi_3 + \tfrac{1}{2}z\varphi_1\varphi_2\,. \tag{3}$$

It is shown in the Appendix that the weight to be associated with the contribution at this point is approximately $P(\boldsymbol{\varphi})D(a\varphi)$, where $P(\boldsymbol{\varphi})$ is the probability of an oscillation $\boldsymbol{\varphi}$ and $D(a\varphi)$ is the density of the original Gaussian peak at a distance $a\varphi$ from its centre. The values of $P(\boldsymbol{\varphi})$ and $D(a\varphi)$ are proportional to

$$P(\boldsymbol{\varphi}) = \exp\left(-\tfrac{1}{2}\Sigma\Sigma\omega^{-1}{}_{ij}\varphi_i\varphi_j\right), \tag{4}$$

and

$$D(a\varphi) = \exp\left(-\tfrac{1}{2}a^2\varphi^2/q^2\right), \tag{5}$$

where $\omega^{-1}{}_{ij}$ is an element of the matrix inverse to ω_{ij}, defined with respect to the arbitrary x, y, z axes, and the summations are for $i, j = 1, 2, 3$.

Thus the x component of the net shift due to the whole angular oscillation specified by ω_{ij} is

$$\varepsilon_x = \int \Delta_x(\boldsymbol{\varphi})P(\boldsymbol{\varphi})D(a\varphi)d\boldsymbol{\varphi} \Big/ \int P(\boldsymbol{\varphi})D(a\varphi)d\boldsymbol{\varphi}\,. \tag{6}$$

Using (2) we can write

$$P(\boldsymbol{\varphi})D(a\varphi) = \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right), \tag{7}$$

where

$$\left.\begin{aligned} A_{11} &= (y^2+z^2)/q^2 + \omega^{-1}{}_{11}\,, \\ A_{12} &= -xy/q^2 + \omega^{-1}{}_{12},\ \text{etc.} \end{aligned}\right\} \tag{8}$$

Since $\Delta_x(\boldsymbol{\varphi})$ is given by (3), we need the result that

$$\begin{aligned} &\int \varphi_i\varphi_j \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right)d\boldsymbol{\varphi} \\ &= A^{-1}{}_{ij}\int \exp\left(-\tfrac{1}{2}\Sigma\Sigma A_{ij}\varphi_i\varphi_j\right)d\boldsymbol{\varphi}\,, \end{aligned} \tag{9}$$

where $A^{-1}{}_{ij}$ is an element of the matrix inverse to A_{ij}. By combining (3), (7) and (9) with (6) the net shift of the electron-density maximum can be found. Reversing the sign, the desired coordinate corrections for a peak observed at (x, y, z) prove to be

$$\left.\begin{aligned}-\varepsilon_x &= \tfrac{1}{2}\{x(A^{-1}{}_{22}+A^{-1}{}_{33})-yA^{-1}{}_{12}-zA^{-1}{}_{13}\}\,,\\ -\varepsilon_y &= \tfrac{1}{2}\{y(A^{-1}{}_{33}+A^{-1}{}_{11})-zA^{-1}{}_{23}-xA^{-1}{}_{12}\}\,,\\ -\varepsilon_z &= \tfrac{1}{2}\{z(A^{-1}{}_{11}+A^{-1}{}_{22})-xA^{-1}{}_{13}-yA^{-1}{}_{23}\}\,.\end{aligned}\right\}\quad(10)$$

We may check that these corrections agree with the previous formula (1) if one of the principal axes of ω_{ij} coincides with the radius. For an atom at $(r, 0, 0)$ and if $\omega_{12}=\omega_{23}=\omega_{13}=0$, the non-zero elements of A_{ij} are

$$A_{11}=1/\omega_{11},\ A_{22}=(r^2/q^2+1/\omega_{22}),\ A_{33}=(r^2/q^2+1/\omega_{33})\,.$$

The corrections then reduce to $-\varepsilon_y=-\varepsilon_z=0$ and

$$-\varepsilon_x=\tfrac{1}{2}\{r(A^{-1}{}_{22}+A^{-1}{}_{33})\}\,,$$

which yields (1) immediately since $s^2=\omega_{22}r^2$ and $t^2=\omega_{33}r^2$.

For the problem in which ω_{11} is large and all other elements of ω_{ij} are negligible and the atom is at $(x, y, 0)$, the only appreciable element of $A^{-1}{}_{ij}$ is

$$A^{-1}{}_{11}=\omega_{11}q^2/(\omega_{11}y^2+q^2)\,.$$

The corrections then reduce to $-\varepsilon_x=-\varepsilon_z=0$ and

$$\begin{aligned}-\varepsilon_y &= -\tfrac{1}{2}y\omega_{11}q^2/(\omega_{11}y^2+q^2)\\ &= \tfrac{1}{2}y\left(\frac{s^2}{1+s^2/q^2}\right),\end{aligned}$$

where $s^2=w_{11}y^2$. This agrees with the intelligent application of (1), when the shift is taken normal to the axis of oscillation rather than towards the molecular centre.

The result for one other special case, which may be useful for planar molecules, is worth quoting. For an atom at $(x, y, 0)$ and when $\omega_{12}=\omega_{23}=\omega_{13}=0$, the x correction is

$$-\varepsilon_x=\tfrac{1}{2}\left\{\frac{1}{x}\left(\frac{q^2\omega_{22}x^2}{q^2+\omega_{22}x^2+\omega_{11}y^2}\right)+\frac{x}{r^2}\left(\frac{\omega_{33}r^2}{1+(\omega_{33}r^2)/q^2}\right)\right\},$$

where $r^2=x^2+y^2$. The first term differs from that suggested by (1) by the addition of $\omega_{11}y^2$ in the denominator; the second term is that expected for the x component of the radial shift due to ω_{33}. The y shift is similar and the z shift is zero.

Any calculations which may have been done with equation (1) will be appreciably in error only if the ω_{ij} tensor is decidedly anisotropic and then only for those atoms whose radii are not roughly normal to the axis of maximum oscillation. The results for benzene (Cox, Cruickshank & Smith, 1958), naphthalene, anthracene (Cruickshank & Sparks, 1960) and β-succinic acid (Broadley *et al.*, 1959) are either exactly as given previously or are altered only negligibly. Even in chrysene (Burns & Iball, 1960), where the two angular oscillations of 17 and 6 deg.^{2} in the plane of the molecule are rather different, the maximum coordinate change is only 0·003 Å; the majority are less than 0·001 Å. The changes are more important in 1,2-diphenyltetrafluoroethane (Cruickshank, Jeffrey & Nyburg, 1959), which is a non-planar molecule and whose principal ω_{ii} of 47·2 and 4 deg.^{2} are markedly anisotropic. The rotational corrections for the bonds C_4–C_5 and C_5–C_6 change from 0·001 to 0·007 Å. The revised bond lengths are C_1'–C_1 1·539 Å (unchanged), C–F 1·359, 1·382 Å (each reduced by 0·003 Å) and mean ring C–C 1·394 Å (an increase of 0·004 Å).

Appendix

The various $\pm\boldsymbol{\phi}$ produce a series of peaks whose maxima are all only a small distance from the equilibrium position. A simple parabolic expansion of each peak shows that the correct weights to be assigned to any such series of adjacent maxima, to give the position of the maximum of the total density *along a given line*, are proportional to $P(\boldsymbol{\phi})S(\boldsymbol{\phi})$, where $P(\boldsymbol{\phi})$ is the probability of the displacements $\pm\boldsymbol{\phi}$ and $S(\boldsymbol{\phi})$ is the second derivative along the given line of the combined $\pm\boldsymbol{\phi}$ peak.

Along the radial line through the equilibrium position, the density from the $\pm\boldsymbol{\phi}$ peak is Gaussian, so that along this line and near the maximum $S(\boldsymbol{\phi})$ is proportional to $D(a\varphi)/q^2$ to the required order of magnitude, where $D(a\varphi)$ is the density of the original Gaussian peak at a distance $a\varphi$ from its centre and q^2 is its breadth parameter. In any other direction perpendicular to a particular vibrational movement, $S(\boldsymbol{\phi})$ has the same value, which is therefore appropriate when there is only one non-zero principal value of ω_{ij} and the shift is towards its axis. The value $P(\boldsymbol{\phi})D(a\varphi)$ is also correct for any direction within the plane when there are only two non-zero principal values of ω_{ij} and the atom is coplanar with their axes. In more general cases, with three non-zero principal values and when the shift is not along the radius, the value of $S(\boldsymbol{\phi})$ will be approximately proportional to $D(a\varphi)/q'^2$ where $q'^2=q^2+(a\varphi)^2\cos^2\alpha$ and α is the angle between the direction of net shift and the motion in the oscillation $\pm\boldsymbol{\phi}$.

It seems a sufficient approximation to take the value $S(\boldsymbol{\phi})=D(a\varphi)/q^2$ in all cases because (*a*) the direction of the net shift is generally unknown in advance, (*b*) it is correct for the two extreme cases of an exactly radial shift and of a shift towards the axis of the single non-zero value of ω_{ij}, and (*c*) $(a\varphi)^2$ is usually smaller than q^2. Since the q^2 factor is common to all $\boldsymbol{\phi}$, we take the weight to be associated with each peak at $\frac{1}{2}\mathbf{a}\varphi^2$ as $P(\boldsymbol{\phi})D(a\varphi)$.

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